

John E. McMurry • Robert C. Fay

General Chemistry: Atoms First

Chapter 18

Hydrogen, Oxygen, and Water

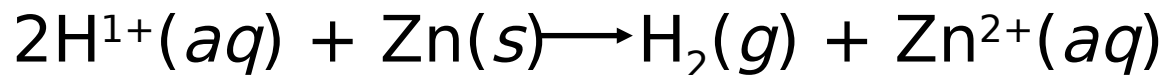
Lecture Notes

Alan D. Earhart

Southeast Community College • Lincoln, NE

Hydrogen

Henry Cavendish (1731–1810) in 1766 is credited with isolating hydrogen in its pure form:

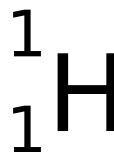


The French chemist Lavoisier called the gas “hydrogen,” meaning “water former,” because it combines with oxygen to form produce water.

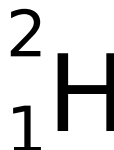
Isotopes of Hydrogen

Three isotopes:

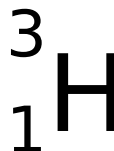
1. Hydrogen-1 (protium):
99.985% abundance



2. Hydrogen-2 (deuterium):
0.015% abundance



3. Hydrogen-3 (tritium):
about $10^{-16}\%$ abundance



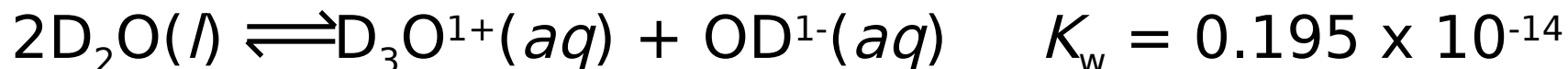
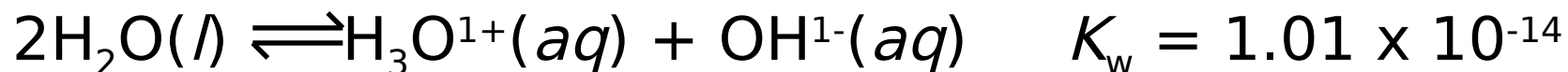
Isotopes of Hydrogen

TABLE 18.1 Properties of Hydrogen Isotopes

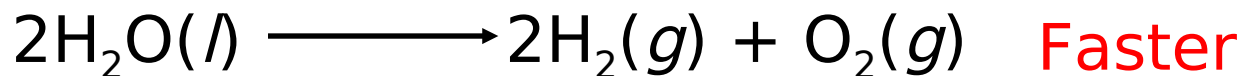
Property	Protium	Deuterium	Tritium
Atomic hydrogen (H)			
Mass, amu	1.0078	2.0141	3.0160
Ionization energy, kJ/mol	1311.7	1312.2	
Nuclear stability	Stable	Stable	Radioactive
Molecular hydrogen (H₂)			
Melting point, K	13.95	18.73	20.62
Boiling point, K	20.39	23.67	25.04
Bond dissociation energy, kJ/mol	435.8	443.3	446.7
Water (H₂O)			
Melting point, °C	0.00	3.82	4.48
Boiling point, °C	100.00	101.42	101.51
Density at 25 °C, g/mL	0.997	1.104	1.214
Dissociation constant K_w at 25 °C	1.01×10^{-14}	0.195×10^{-14}	$\sim 0.06 \times 10^{-14}$

Isotopes of Hydrogen

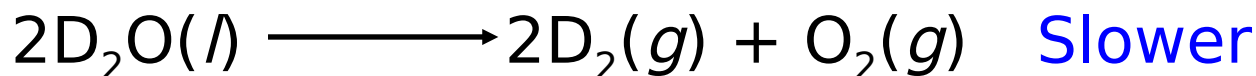
Isotope Effects



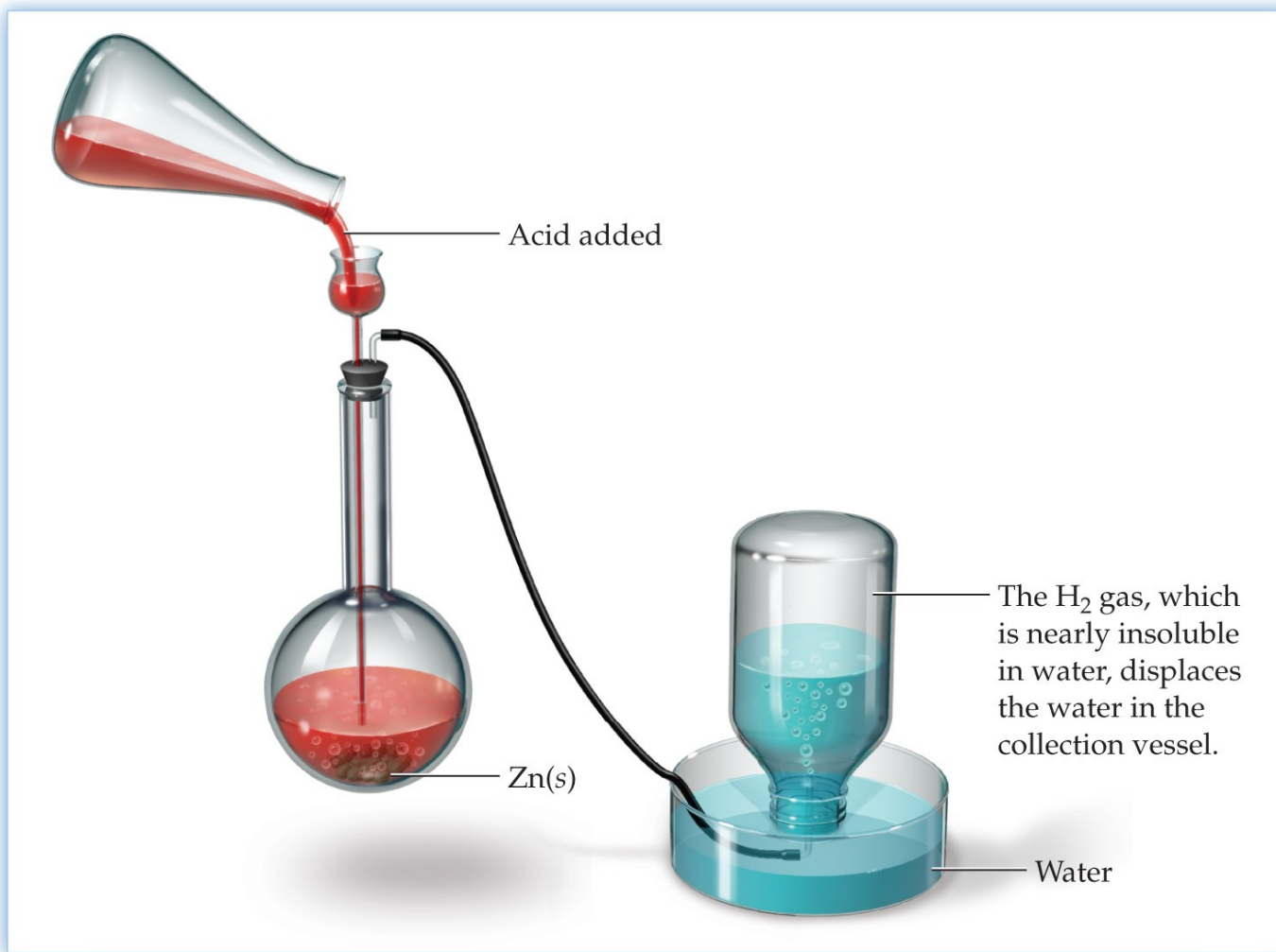
Electrolysis



Electrolysis

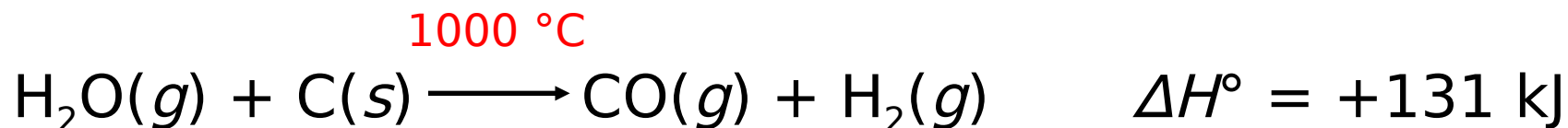
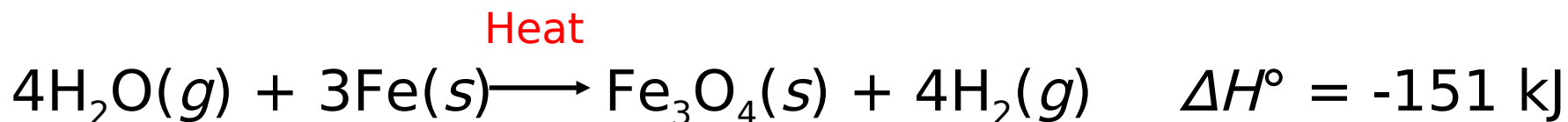


Preparation and Uses of



Preparation and Uses of Hydrogen

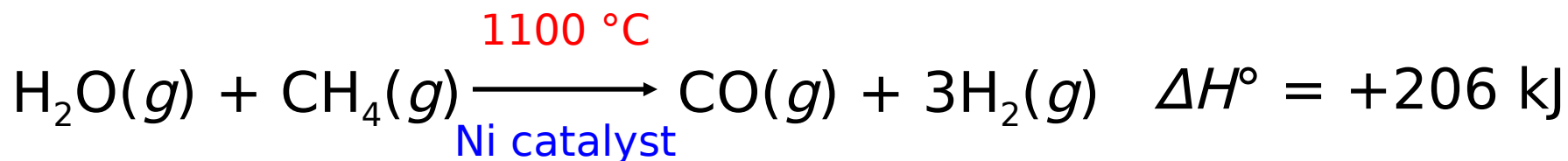
All large-scale, industrial methods for producing hydrogen use an inexpensive reducing agent such as hot iron, carbon, or methane (natural gas):



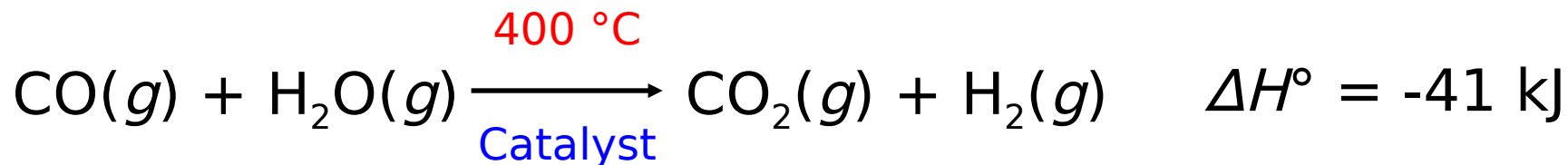
Preparation and Uses of Hydrogen

Currently, the most important industrial method for producing hydrogen is the three-step, **steam-hydrocarbon re-forming process**.

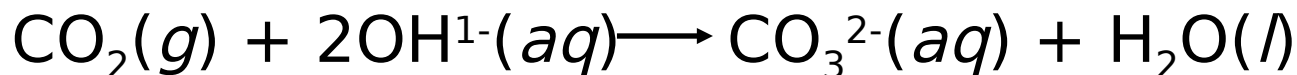
1. First Step: The production of *synthesis gas*:



2. Second Step: The *water-gas shift reaction*:

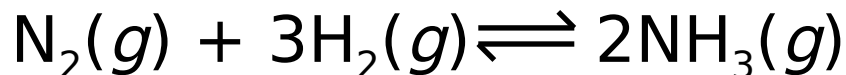


3. Third Step: Removal of excess carbon dioxide:

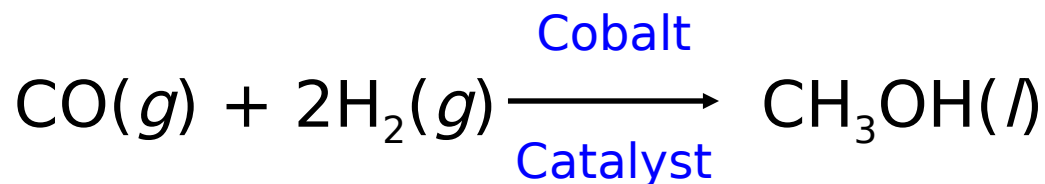


Preparation and Uses of Hydrogen

Haber process:



Methanol synthesis:



Reactivity of Hydrogen

Alkali-metal-like reaction to form hydrogen ion:



Halogen-like reaction to form hydride ion:



While hydrogen gas is relatively unreactive at room temperature, gas mixtures with as little as 4% hydrogen by volume in air are highly exothermic and potentially explosive:



Binary Hydrides

The group 1A and the heavier group 2A hydrides, shown in blue, are ionic.

The other main-group hydrides, shown in red, are covalent. The change in bond type, however, is gradual and continuous.

Transition metal hydrides (not shown) are classified as metallic.

The letter "d" indicates decomposition rather than melting on heating to the indicated temperature.

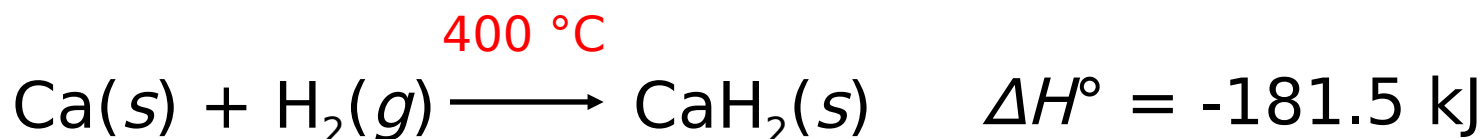
1 1A	2 2A						18 8A
LiH 692	BeH ₂ d 250		13 3A	14 4A	15 5A	16 6A	17 7A
NaH d 425	MgH ₂ d 327		B ₂ H ₆ -165	CH ₄ -182	NH ₃ -78	H ₂ O 0	HF -83
KH 619	CaH ₂ 1000		AlH ₃ d 150	SiH ₄ -185	PH ₃ -134	H ₂ S -86	HCl -114
RbH d ~170	SrH ₂ 1050		GaH ₃ -15	GeH ₄ -165	AsH ₃ -116	H ₂ Se -66	HBr -87
CsH 528	BaH ₂ 1200		InH ₃ (?)	SnH ₄ -146	SbH ₃ -88	H ₂ Te -49	HI -51
			TlH ₃ (?)	PbH ₄	BiH ₃ -67	H ₂ Po	HAt

The existence of InH₃ and TlH₃ is uncertain.

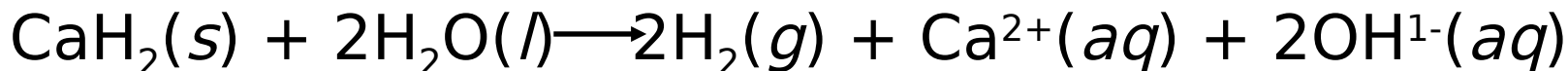
Binary Hydrides

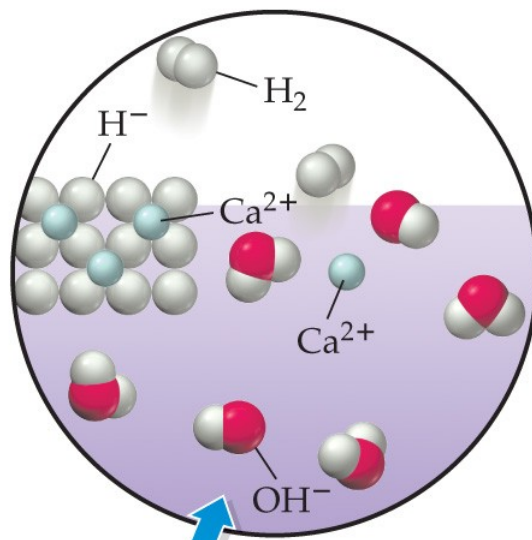
Ionic Hydrides

Saltlike, high melting, white, crystalline compounds formed by the alkali metals and the heavier alkaline earth metals Ca, Sr, and Ba:



The hydride ion is a good proton acceptor (Brønsted-Lowry base):





Binary Hydrides

Covalent Hydrides

Common hydrides of nonmetallic elements, such as diborane (B_2H_6), methane (CH_4), ammonia (NH_3), water (H_2O), and hydrogen halides (HX ; $\text{X} = \text{F}, \text{Cl}, \text{Br},$ or I).

In general, their intermolecular forces are relatively weak so they exist as gases or volatile liquids at ordinary temperatures.

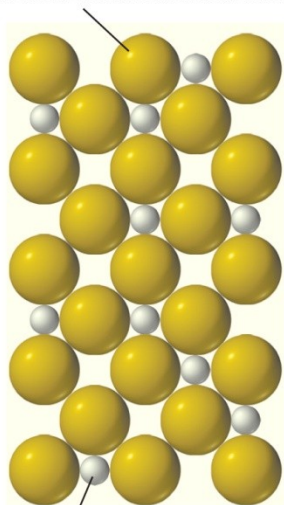
Binary Hydrides

Metallic Hydrides

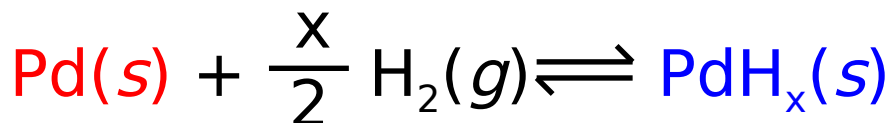
Formed by the reaction of the lanthanides and actinide metals and certain *d*-block transition metals with variable amounts of hydrogen with the general

formula MH_x

The metal atoms (larger spheres) have a face-centered cubic structure.



The hydrogen atoms (smaller spheres) occupy interstices (holes) between the metal atoms.

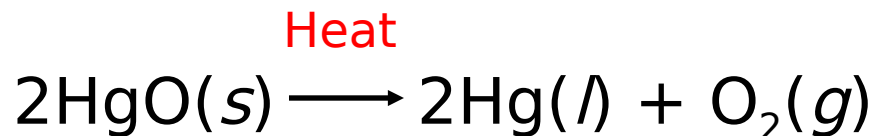


Favored at
higher
temperature

Favored at
lower
temperature

Oxygen

Joseph Priestly and Karl Wilhelm Scheele are credited for isolating and characterizing oxygen between 1771 and 1774:



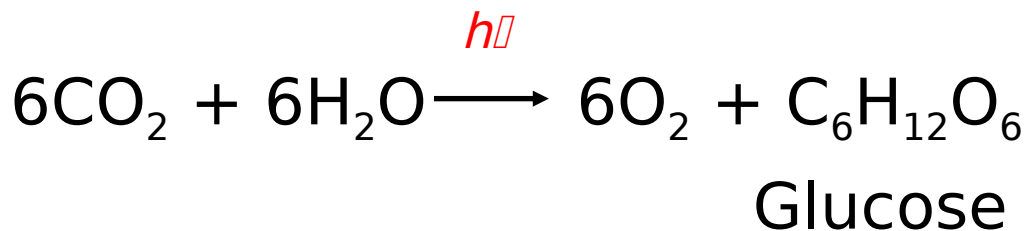
Priestly called the gas “dephlogistated air.”
Lavoisier called it “oxygen” which means “acid former.”

Gaseous O_2 condenses at $-183\text{ }^\circ\text{C}$ to form a pale blue liquid and freezes at -219 to give a pale blue solid.

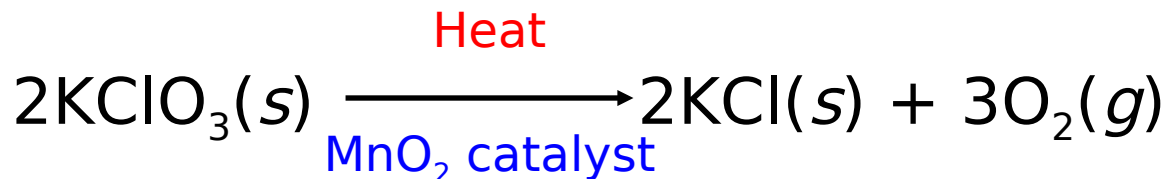
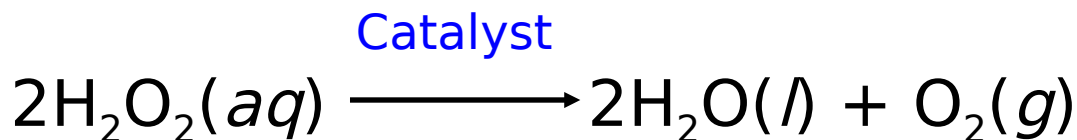
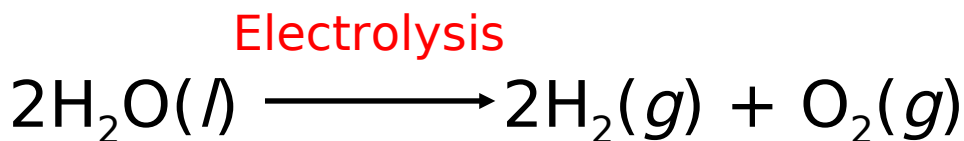


Preparation and Uses of Oxygen

Photosynthesis constantly replaces used oxygen:

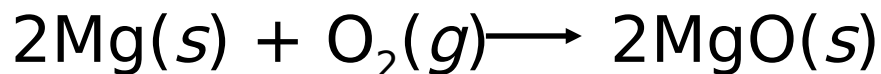
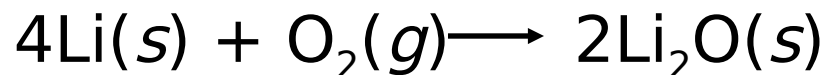


Small amounts of oxygen can be generated in the lab:



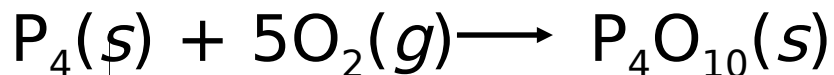
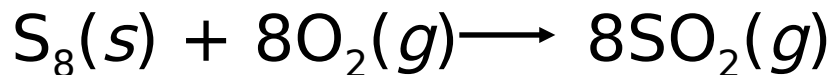
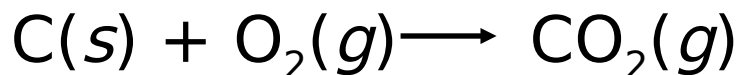
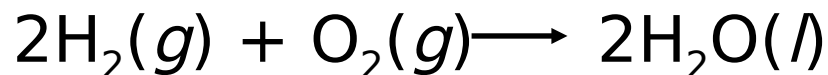
Reactivity of Oxygen

Oxygen will react with active metals, such as lithium and magnesium, to give *ionic oxides*:



Reactivity of Oxygen

With nonmetals such as hydrogen, carbon, sulfur, and phosphorus, oxygen forms *covalent oxides*:



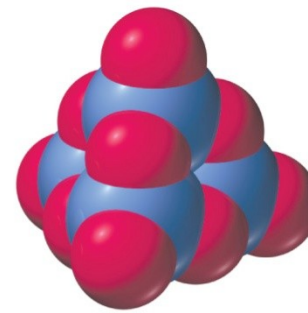
Water



Carbon dioxide



Sulfur dioxide

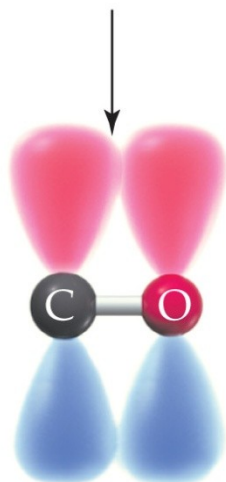


Tetraphosphorus decoxide

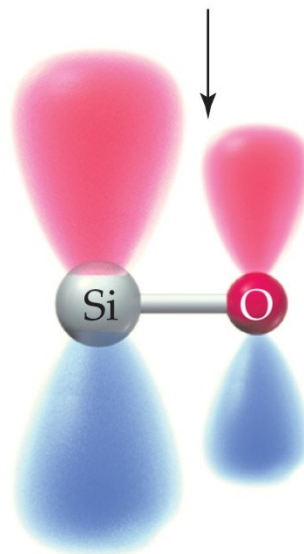
Reactivity of Oxygen

In covalent compounds, oxygen often forms a double bond with carbon and oxygen. However, with larger atoms double bond formation is less common.

Good overlap: With a second-row atom, such as carbon, oxygen forms a strong π bond.



Poor overlap: With a larger atom, such as silicon, oxygen tends not to form π bonds because the longer Si–O distance and the larger, more diffuse silicon orbitals result in poor π overlap.



Reactivity of Oxygen



Magnesium metal burns in oxygen with a bright white flame, producing a white smoke of solid magnesium oxide, MgO .



Hot, molten sulfur burns in oxygen with a blue flame, forming gaseous sulfur dioxide, SO_2 .



White phosphorus spontaneously inflames in oxygen, yielding an incandescent white smoke of solid P_4O_{10} .

Oxides

Increasing acidic character
Increasing covalent character

1 1A → 18 8A

1 1A		13 3A 14 4A 15 5A 16 6A 17 7A					18 8A
	2 2A						
Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₅			
Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇	
K ₂ O	CaO	Ga ₂ O ₃	GeO ₂	As ₂ O ₅	SeO ₃	Br ₂ O ₅	
Rb ₂ O	SrO	In ₂ O ₃	SnO ₂	Sb ₂ O ₅	TeO ₃	I ₂ O ₅	
Cs ₂ O	BaO	Tl ₂ O ₃	PbO ₂	Bi ₂ O ₅			

■ = Basic oxides
■ = Amphoteric oxides
■ = Acidic oxides

Increasing basic character
 Increasing ionic character

Oxides

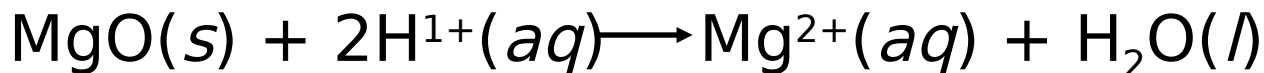
Basic Oxides

Also called *basic anhydrides*. These compounds are *ionic* and formed by metals on the left side of the periodic table.

Water-soluble basic oxides dissolve in water:



Water-insoluble basic oxides dissolve in strong acids:

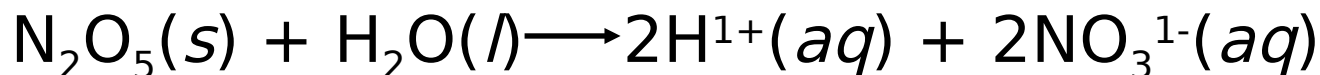


Oxides

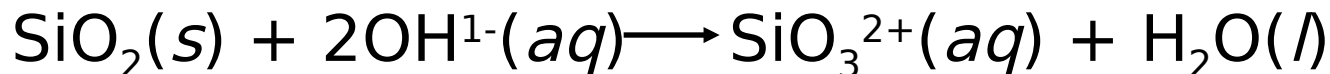
Acidic Oxides

Also called *acid anhydrides*. These compounds are *covalent* and formed by nonmetals on the right side of the periodic table.

Water-soluble acidic oxides dissolve in water:



Water-insoluble basic oxides dissolve in strong bases:

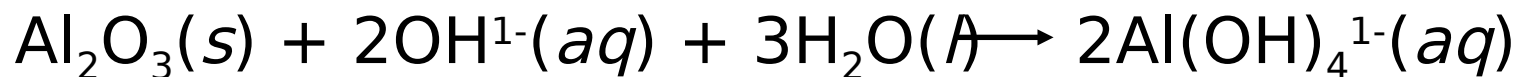
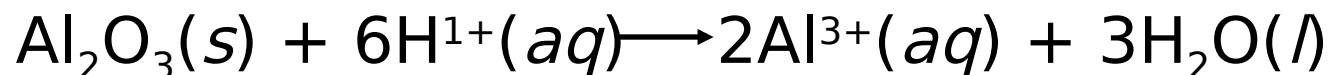


Oxides

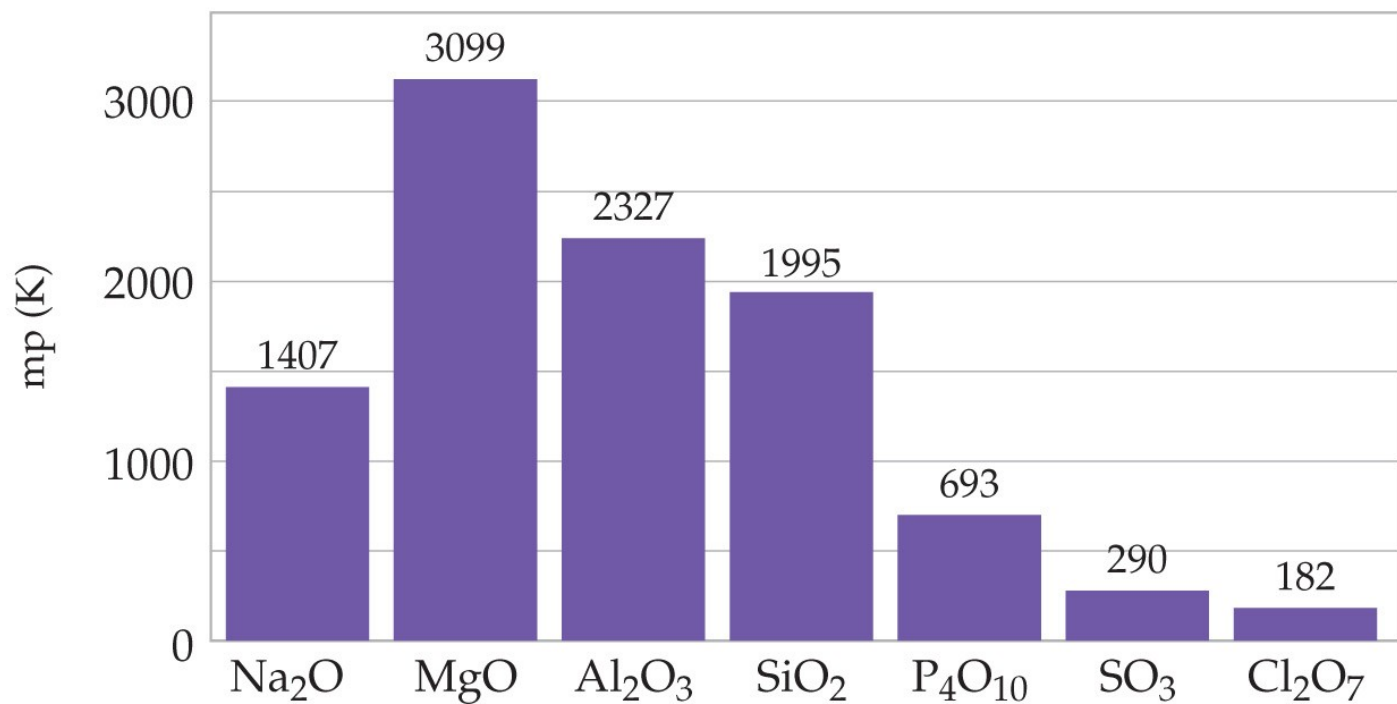
Amphoteric Oxides

These compounds exhibit both acidic and basic properties.

For example, Al_2O_3 is insoluble in water, but it dissolves both in strong acids and strong bases:



Oxides



Ionic oxides: Extended three-dimensional structures

Increasing covalent character

Increasing ionic character

Covalent oxides: Discrete molecular structures

Peroxides and Superoxides

When some of the group 1A and group 2A metals are heated in excess oxygen, they will form either peroxides, such as Na_2O_2 and BaO_2 , or superoxides, such as KO_2 , RbO_2 , and CsO_2 .

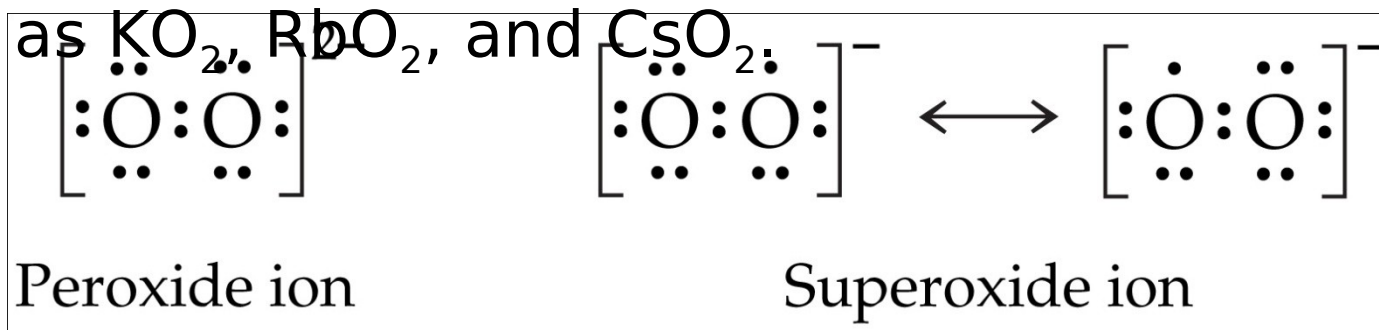
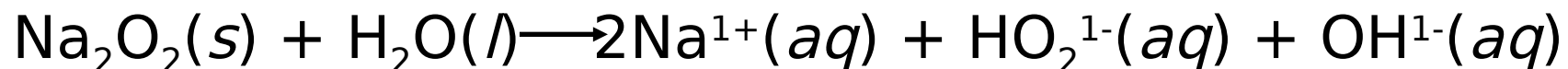


TABLE 18.2 Bond and Magnetic Properties of Diatomic Oxygen Species

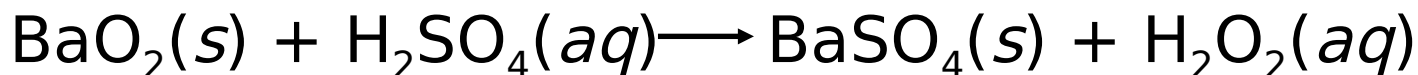
Species	Number of π^*_{2p} Electrons	Number of Unpaired Electrons	Bond Order	Bond Length (pm)	Magnetic Properties
O_2	2	2	2	121	Paramagnetic
O_2^-	3	1	1.5	128	Paramagnetic
O_2^{2-}	4	0	1	149	Diamagnetic

Peroxides and Superoxides

The peroxide ion is a basic anion:

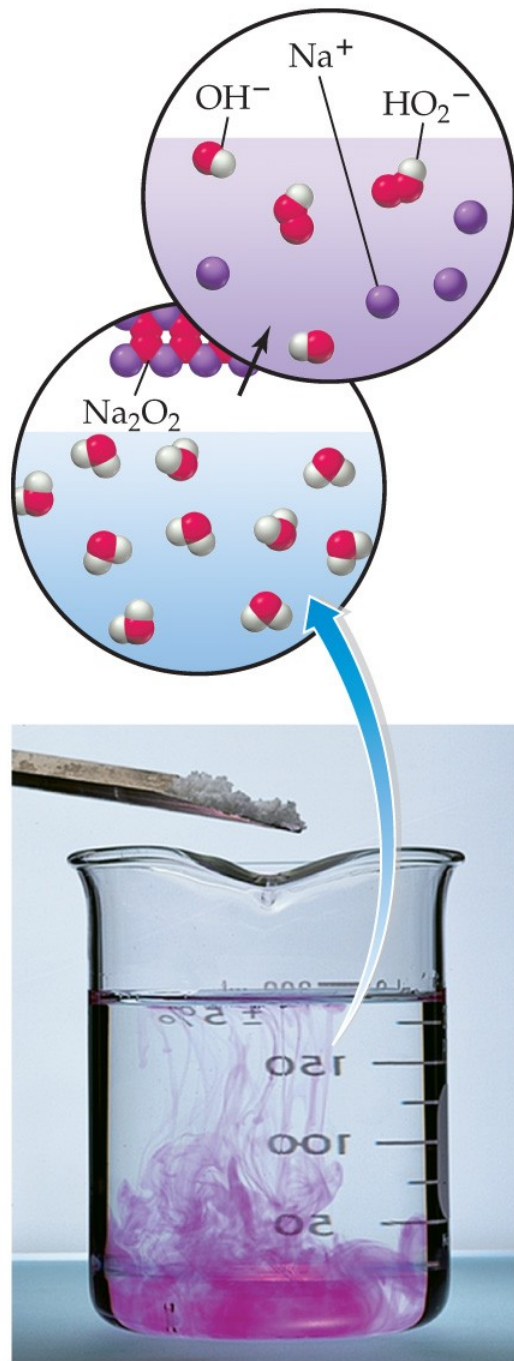


Peroxides will react with strong acids:

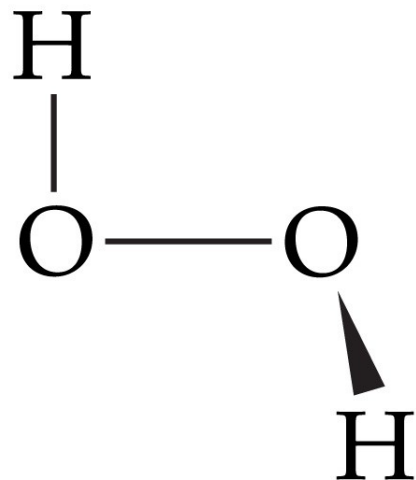


Superoxides can dissolve in water:

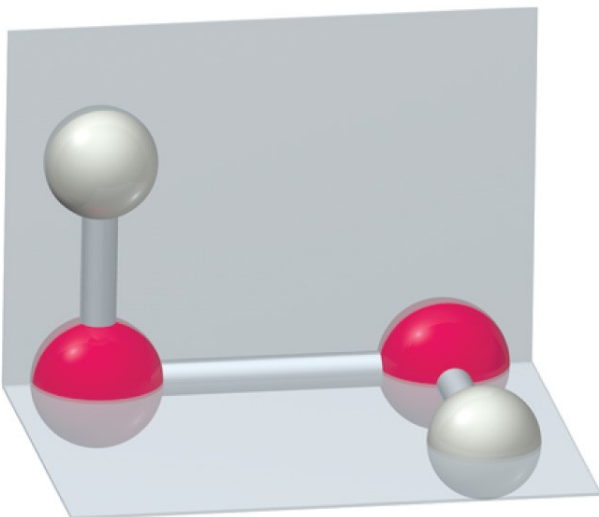




Hydrogen Peroxide

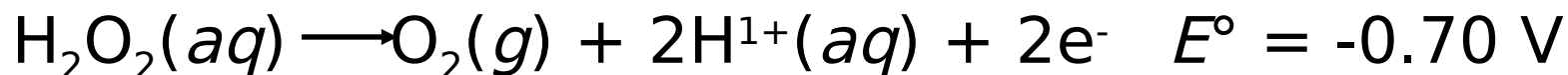


Pure hydrogen peroxide freezes at -0.4 °C and is estimated to boil at 150 °C.



Hydrogen Peroxide

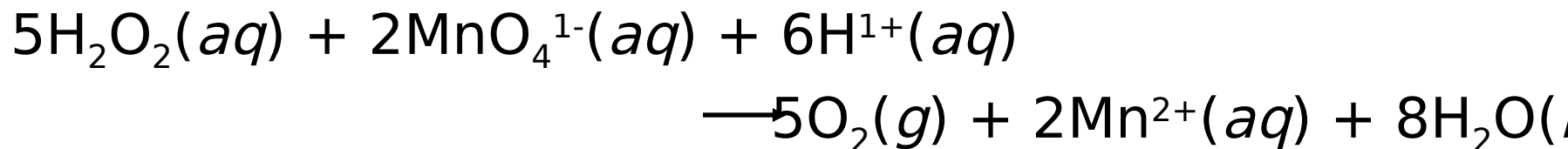
Hydrogen peroxide is both a strong reducing agent and a strong oxidizing agent:



As an oxidizing agent:



As a reducing agent:



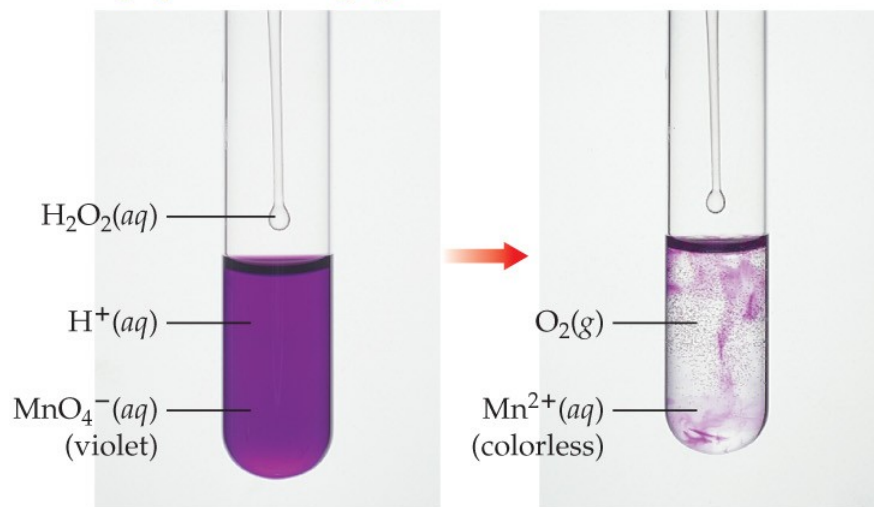
Hydrogen Peroxide

H_2O_2 as an oxidizing agent



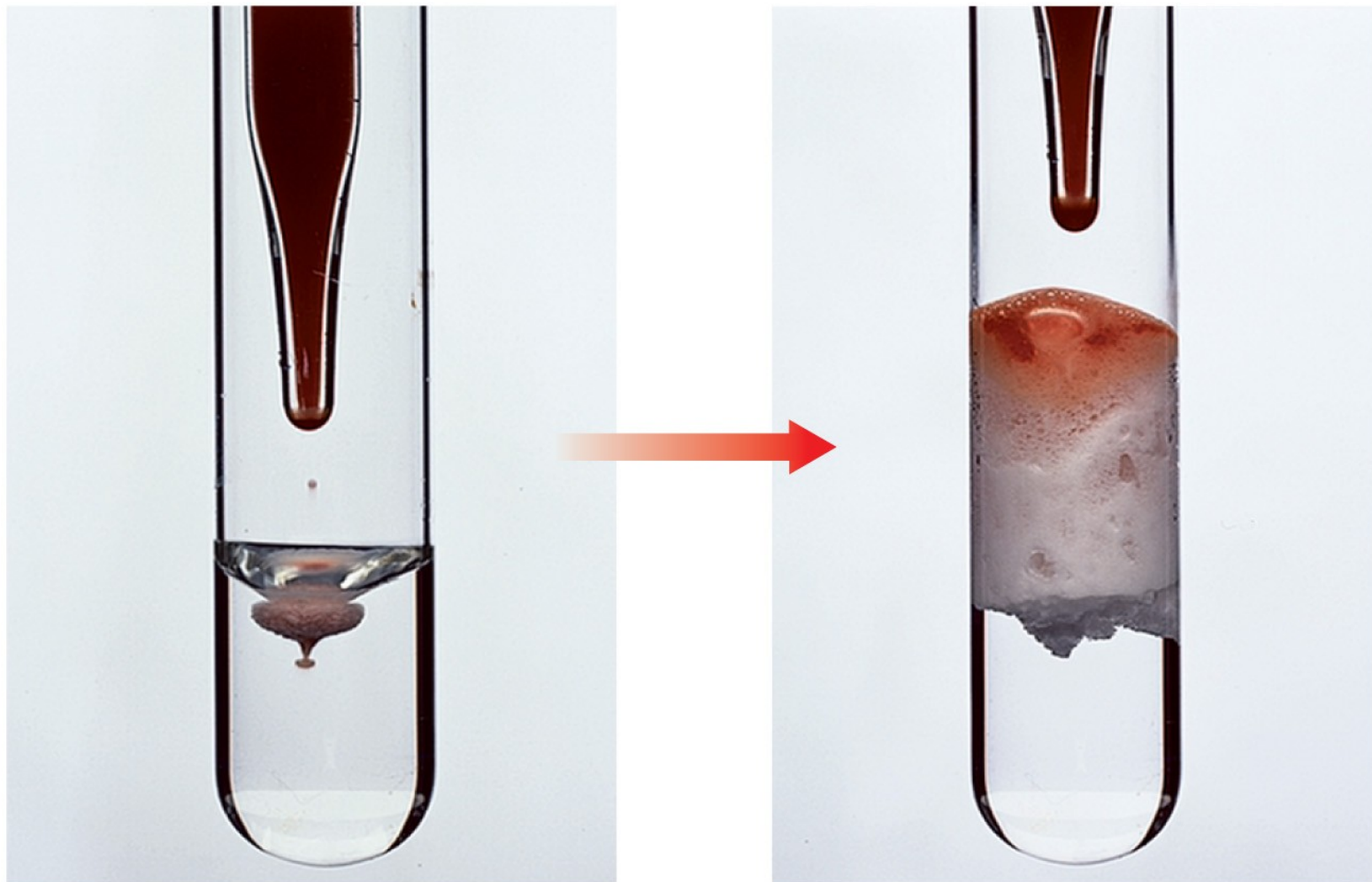
Addition of a colorless aqueous solution of H_2O_2 to a colorless acidic solution of NaBr produces a yellow-orange color due to formation of bromine, Br_2 .

H_2O_2 as a reducing agent



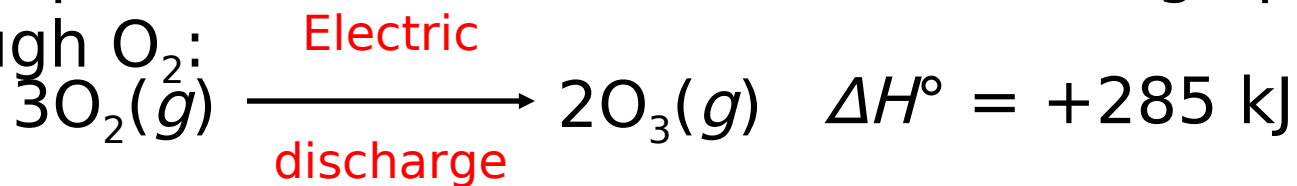
Addition of aqueous H_2O_2 to a violet acidic solution of KMnO_4 produces bubbles of O_2 gas and decolorizes the solution as the violet MnO_4^- ion is converted to the nearly colorless Mn^{2+} ion.

The disproportionation of H_2O_2

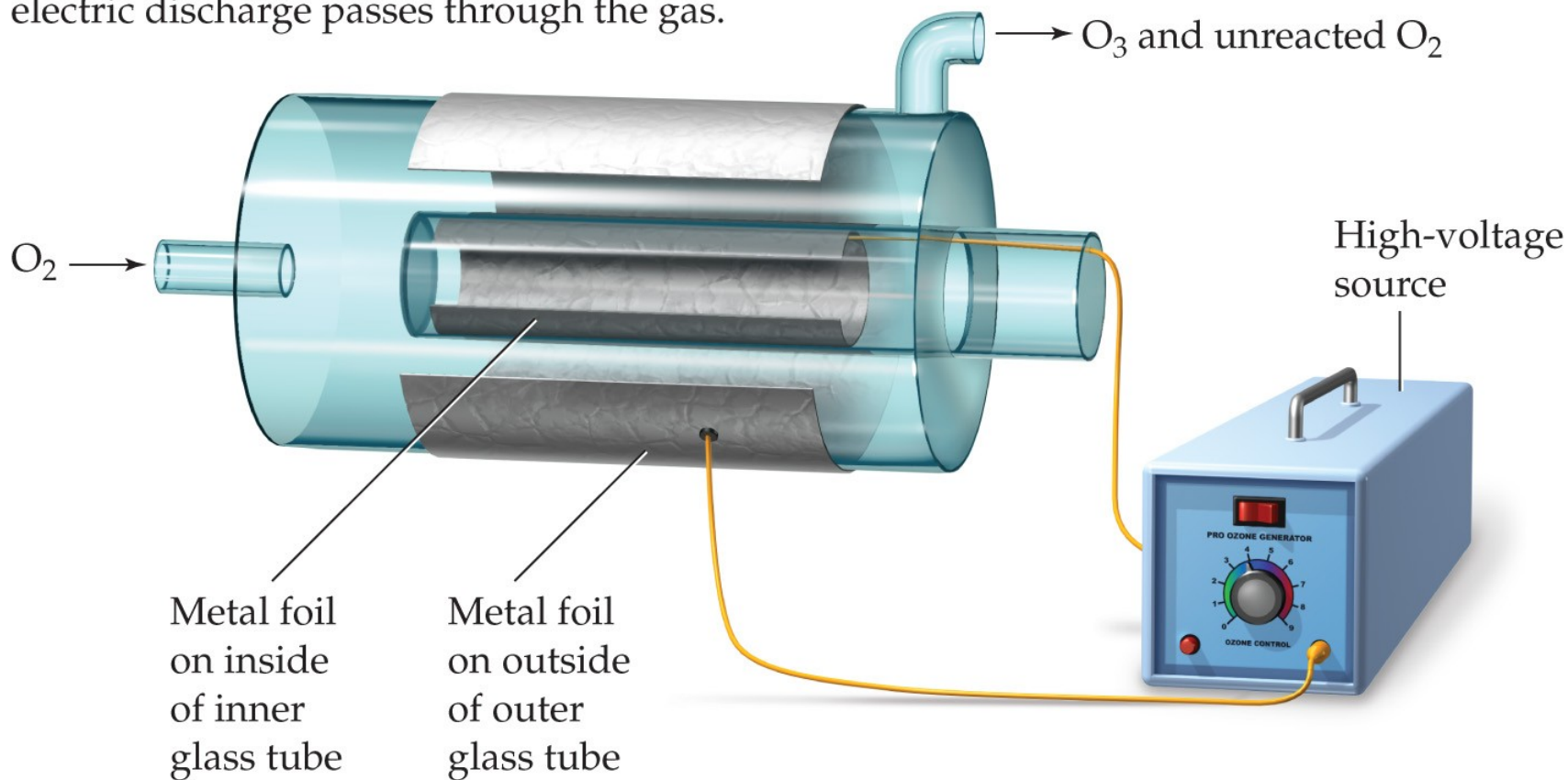


Ozone

Oxygen exists in two allotropes: ordinary oxygen (O_2) and ozone (O_3). Ozone is a toxic, pale blue gas and is produced when an electric discharge passes through O_2 :



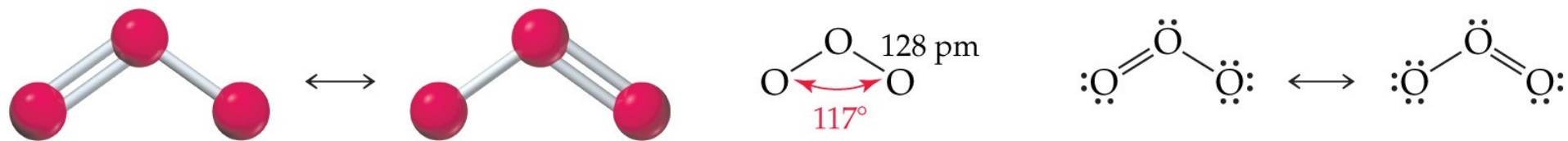
A stream of O_2 gas flows through the ozonizer tube and is partially converted to O_3 when an electric discharge passes through the gas.



Ozone

While dilute gaseous ozone decomposes slowly, the concentrated gas, liquid ozone (bp $-111\text{ }^{\circ}\text{C}$), and solid ozone (mp $-193\text{ }^{\circ}\text{C}$) can all decompose explosively.

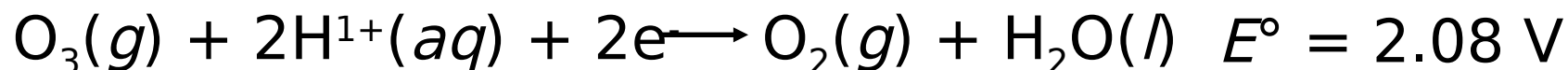
Two resonance structures are needed to explain the structure of the ozone molecule because the two O-O bonds have equal lengths:



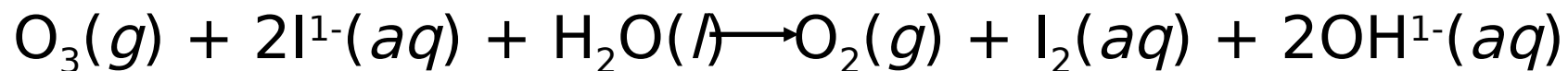
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Ozone

Ozone is an extremely powerful oxidizing agent:



A standard method for detecting ozone in polluted air is to pass the air through a basic solution of potassium iodide that contains a starch indicator:



Starch and iodine
combine to form a
deep blue complex.



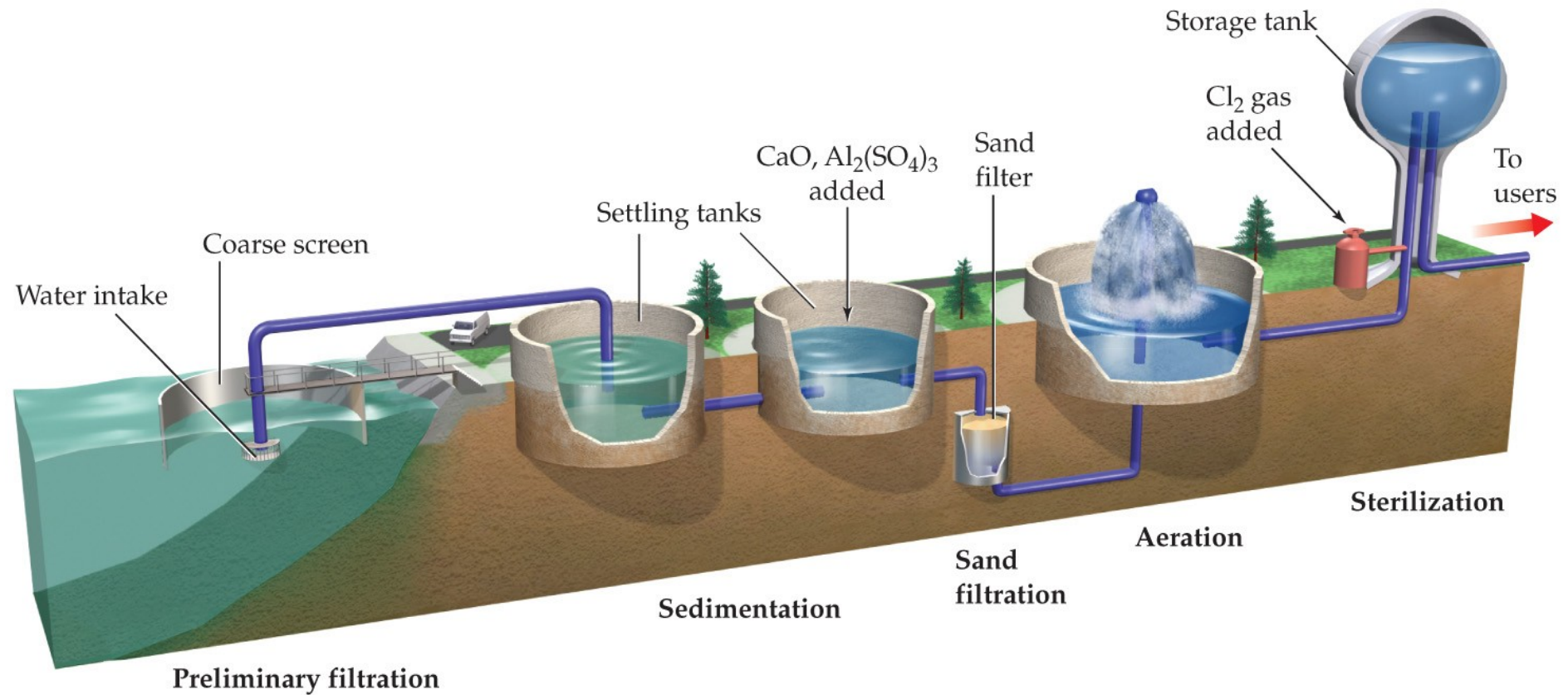
Water

TABLE 18.3 Major Ionic Constituents of Seawater

Ion	g/kg of Seawater
Cl^-	19.0
Na^+	10.5
SO_4^{2-}	2.65
Mg^{2+}	1.35
Ca^{2+}	0.40
K^+	0.38
HCO_3^-	0.14
Br^-	0.065

It's estimated that there is approximately $1.35 \times 10^{18} \text{ m}^3$ of water in the oceans, which accounts for 97.3% of the Earth's total water supply. Freshwater lakes and rivers account for less than 0.01% of the total (about $1.26 \times 10^{14} \text{ m}^3$).

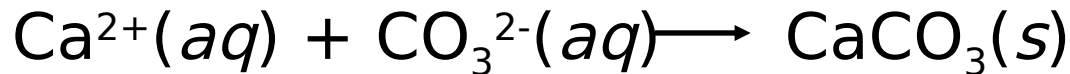
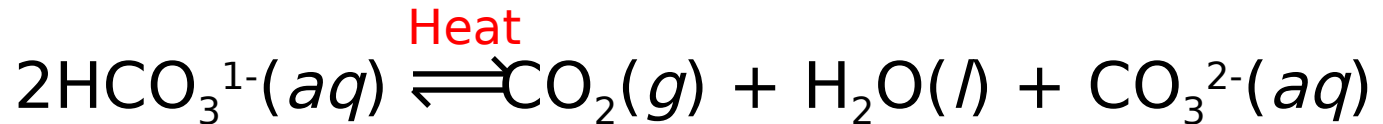
Water



Water

Water that contains appreciable concentrations of doubly charged ions such as Ca^{2+} , Mg^{2+} , and Fe^{2+} is called *hard water*.

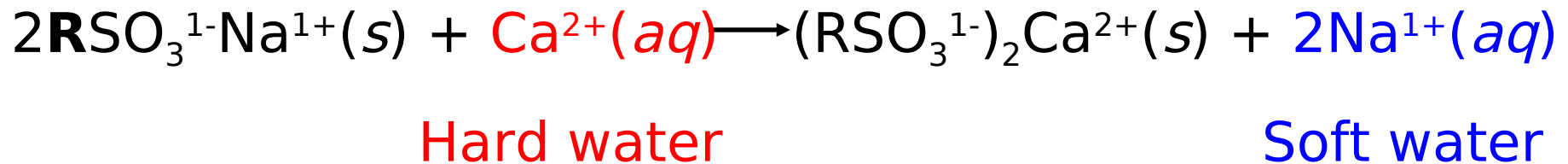
Boiler scale is made of metal carbonate precipitates.



Water

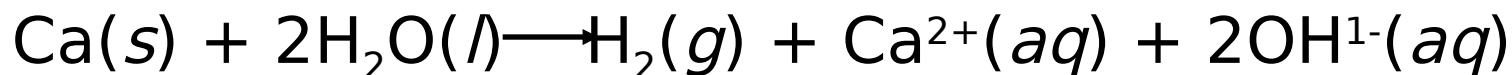
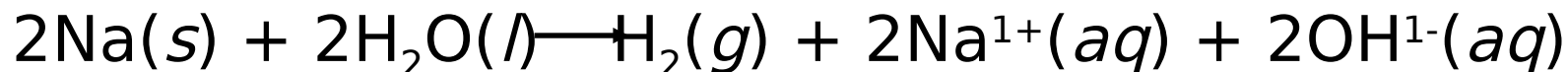
Ion exchange is a process that replaces Ca^{2+} and Mg^{2+} with Na^{1+} :

Resin (**R**) with SO_3^{2-}
and Na^{1+} attached

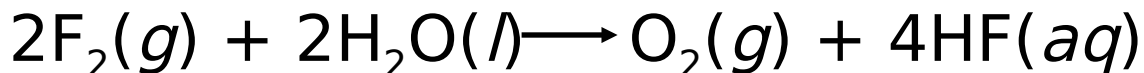


Reactivity of Water

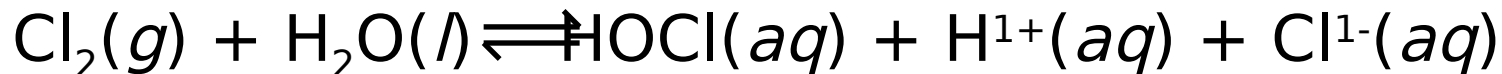
Water is reduced by alkali and the heavier alkaline earth metals:



Fluorine is the only element able to oxidize water:

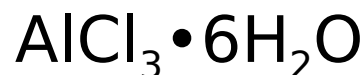
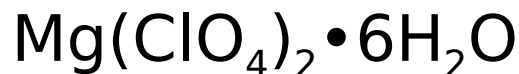


Cl_2 , Br_2 , and I_2 disproportionate in water:



Hydrates

Hydrates: Solid compounds that contain water molecules.



Compounds that absorb water from the air are **hygroscopic** and can be used as drying agents.

